Real-time Measurements of the Mixing State of Elemental Carbon

Prof. Kim Prather
Dept. of Chemistry and Biochemistry
Scripps Institution of Oceanography
University of California, San Diego

Questions

* What are the limits in our ability to measure freshly emitted and ambient BC?

* What are the limits in our ability to determine the sizes and chemical composition of aerosols emitted by BC sources?

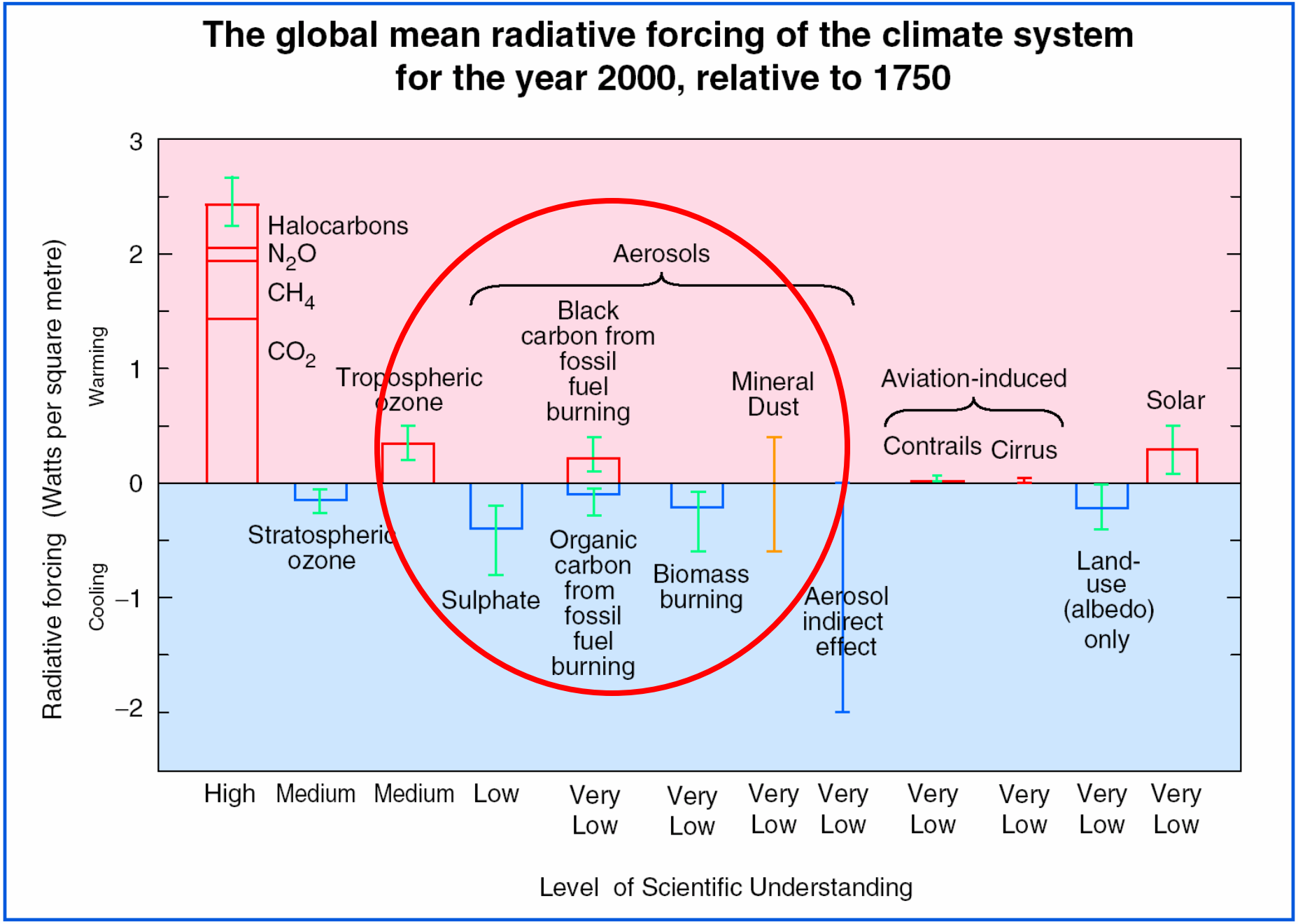
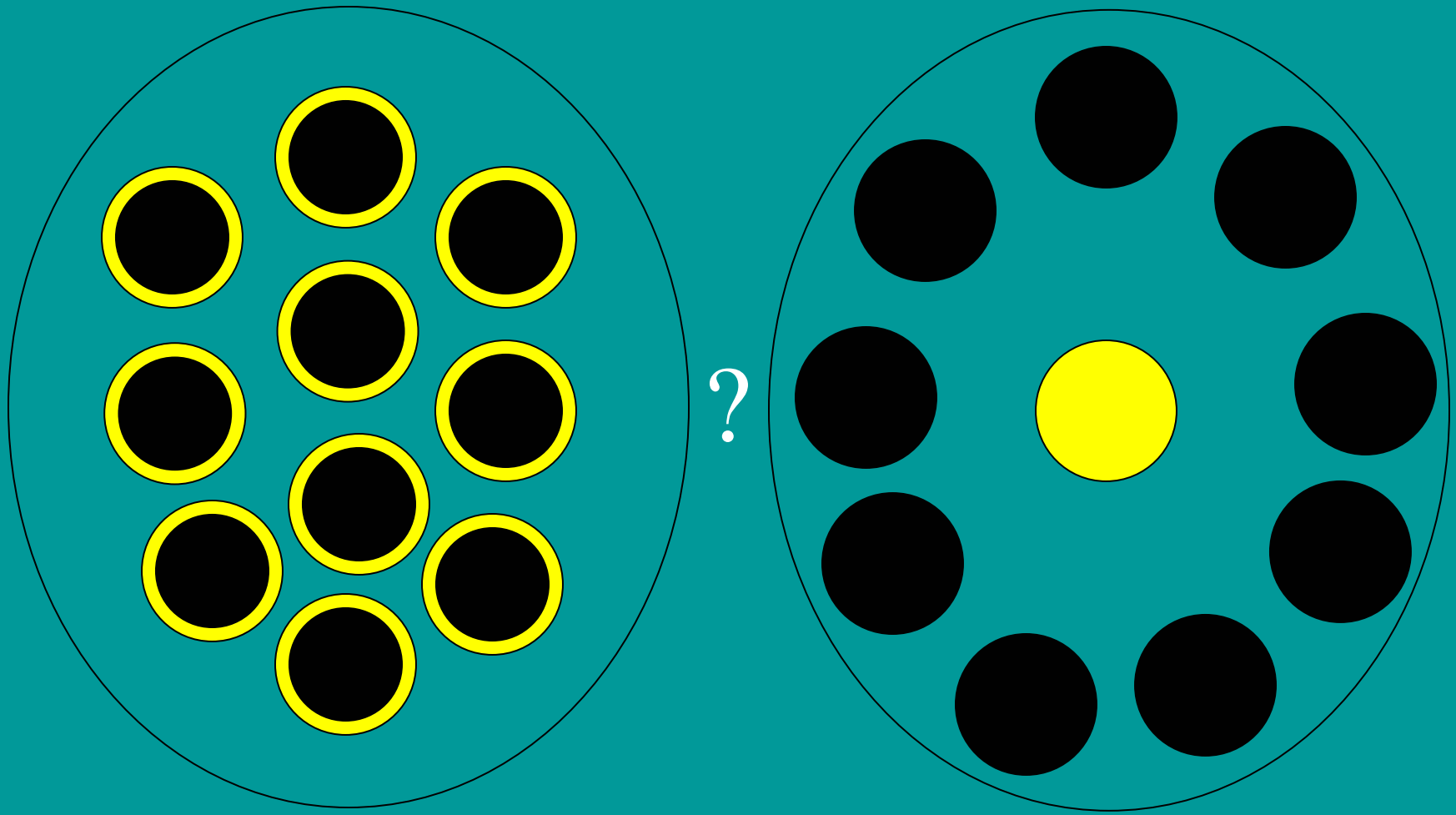


Figure 3: Many external factors force climate change.

Chemical Associations (Mixing State)



10% sulfate (●) 90% Elemental Carbon (●)

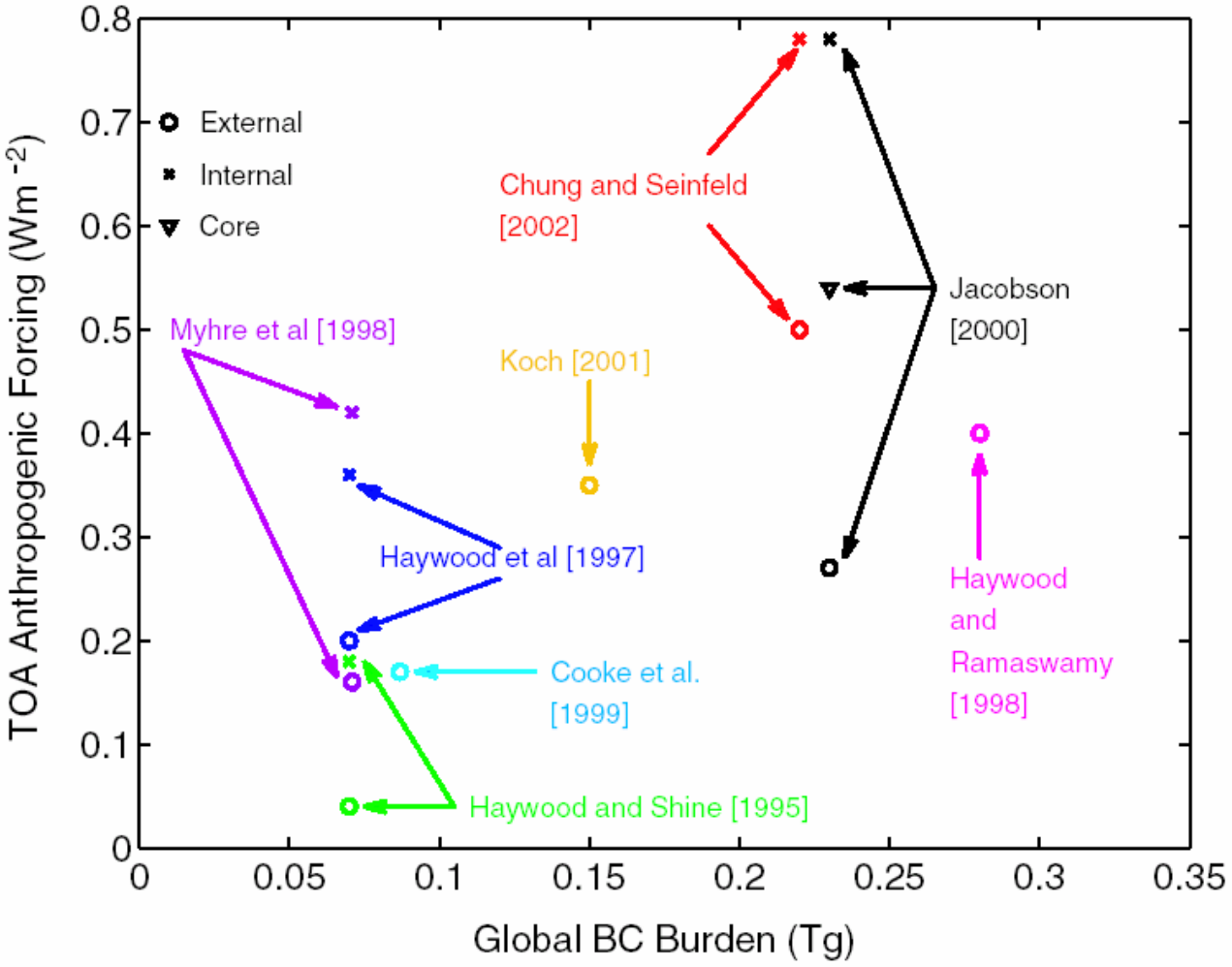


Figure 21. Comparison of BC radiative forcing predictions versus BC global burden by various authors. The color of the data points is coded to the authors, and their shapes correspond to the assumptions made about the mixing state of the aerosols.

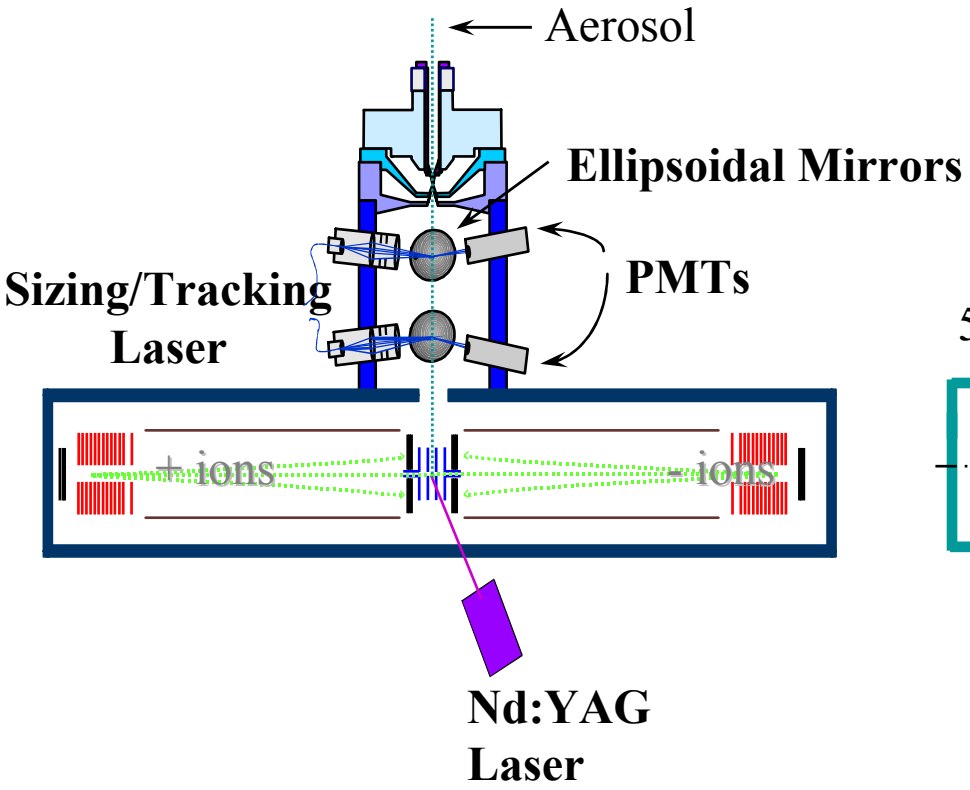
Chung and Seinfeld, JGR 107, D19, 4407, doi:10.1029/2001JD001397, 2002

Single Particle Mass Spectrometry (ATOFMS)

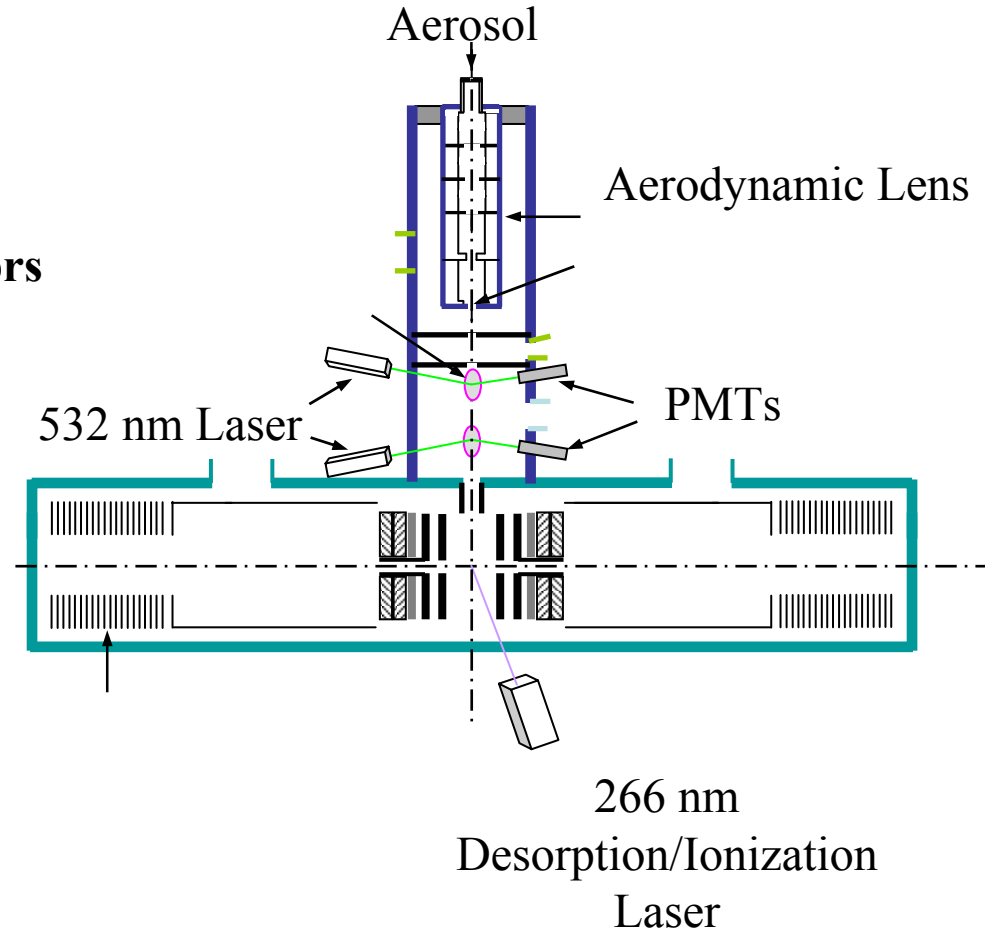
- Direct measure of mixing state (chemical associations)
- High temporal resolution
- Millions of particles (statistics)
- Size-resolved composition

- Output: Size-resolved number fractions of major PM sources
- Ultimate goal: Determine the role of specific PM sources on climate forcing and regional variability

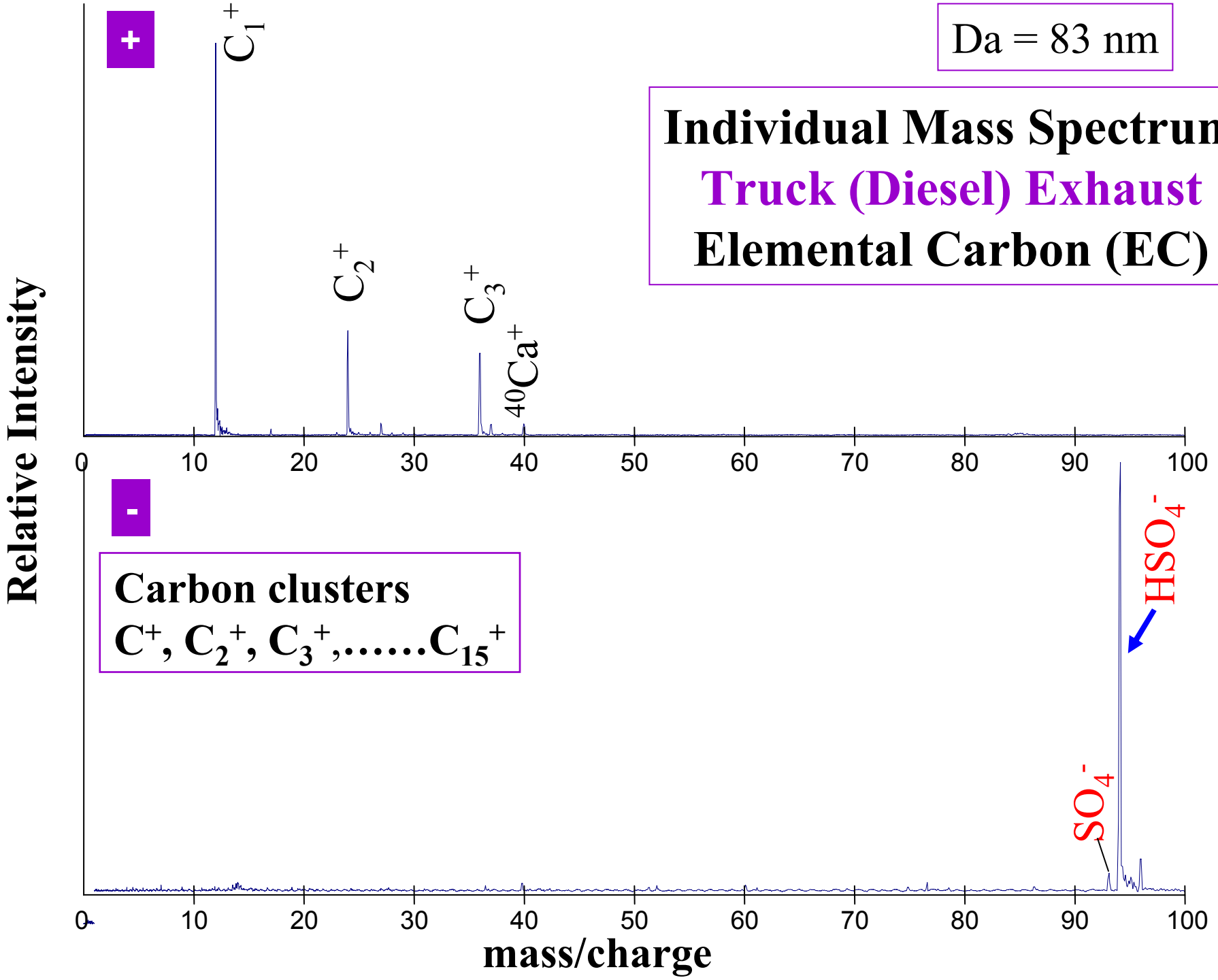
ATOFMS (0.2 – 3 μm)

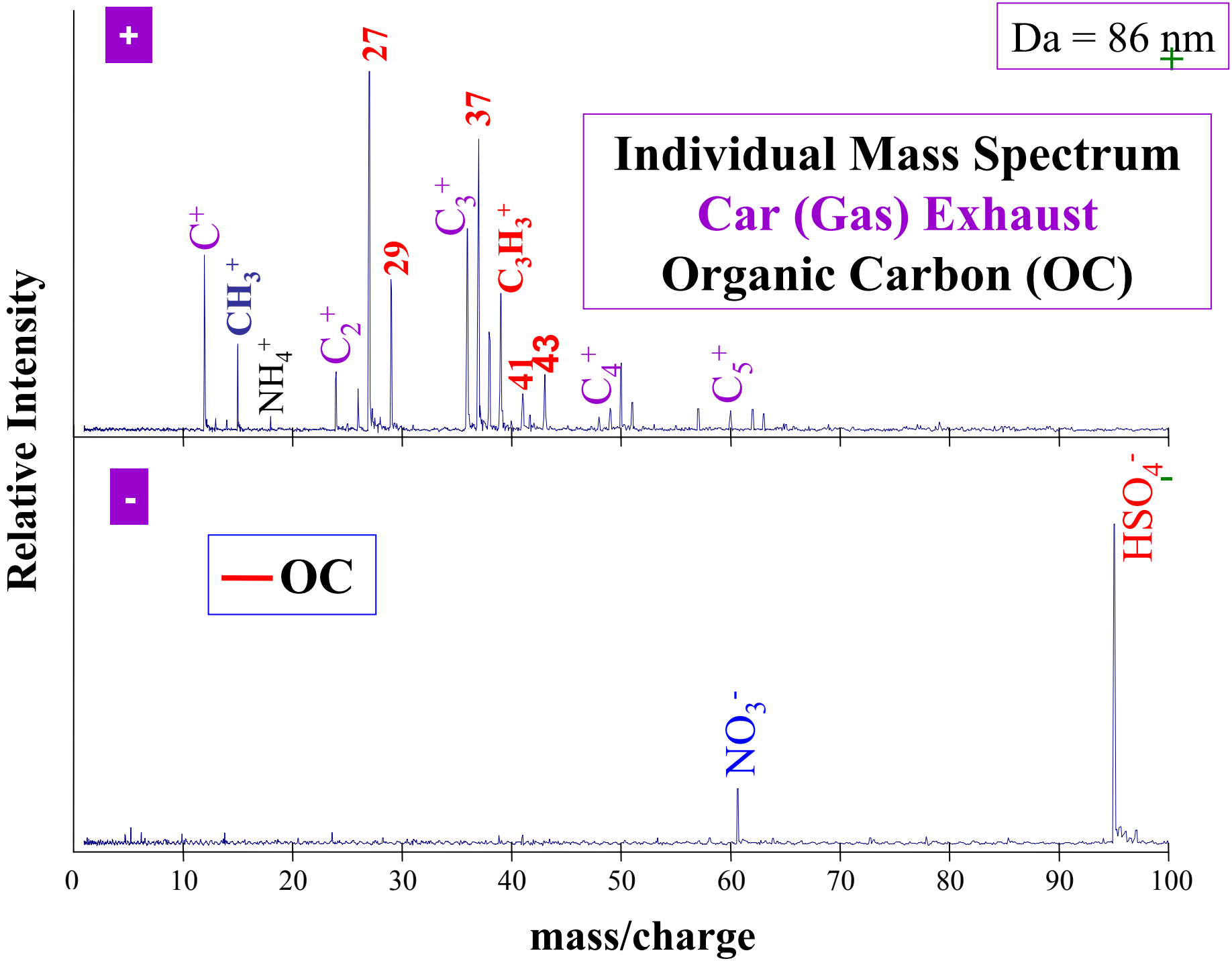


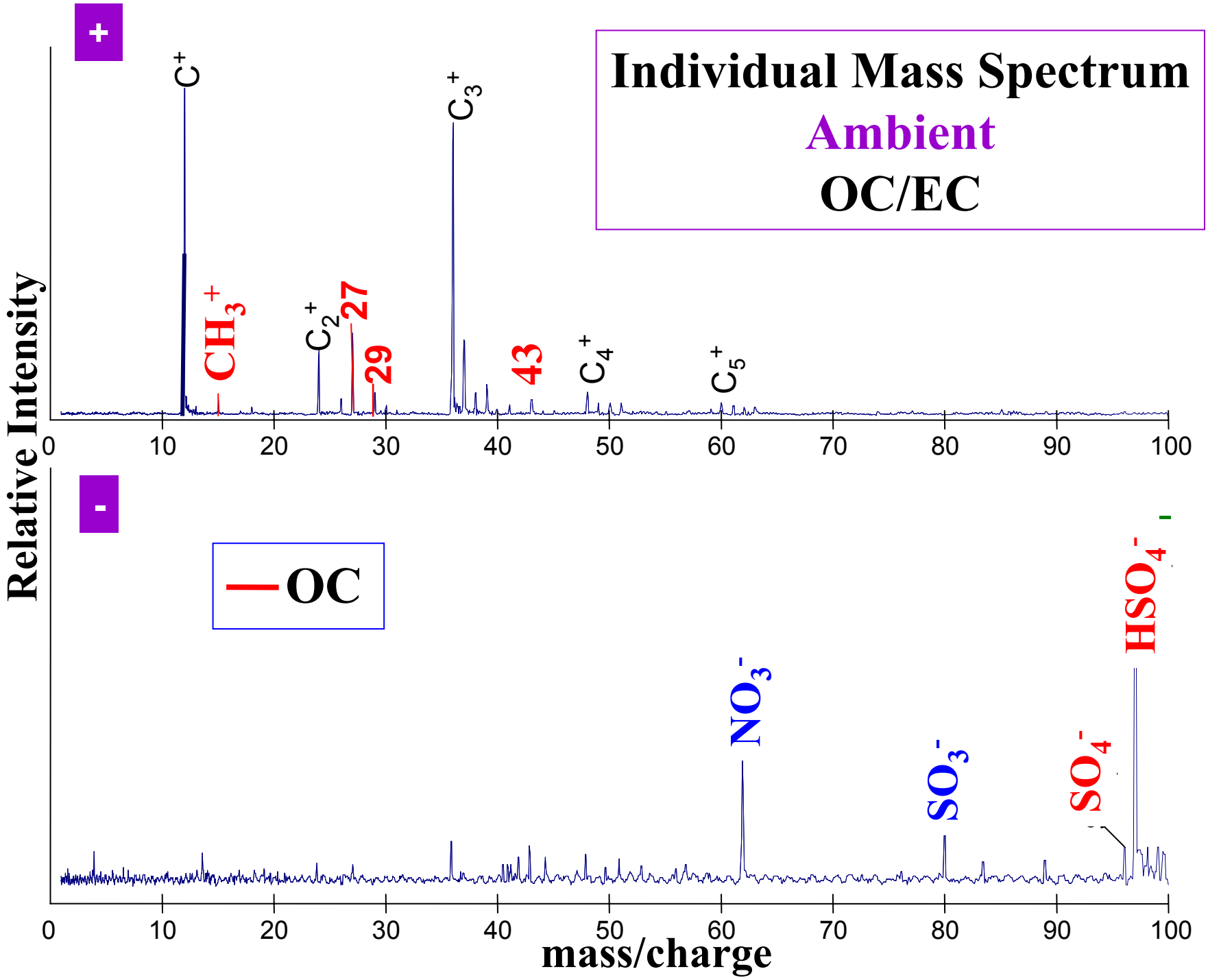
UF ATOFMS (50 – 300 nm)



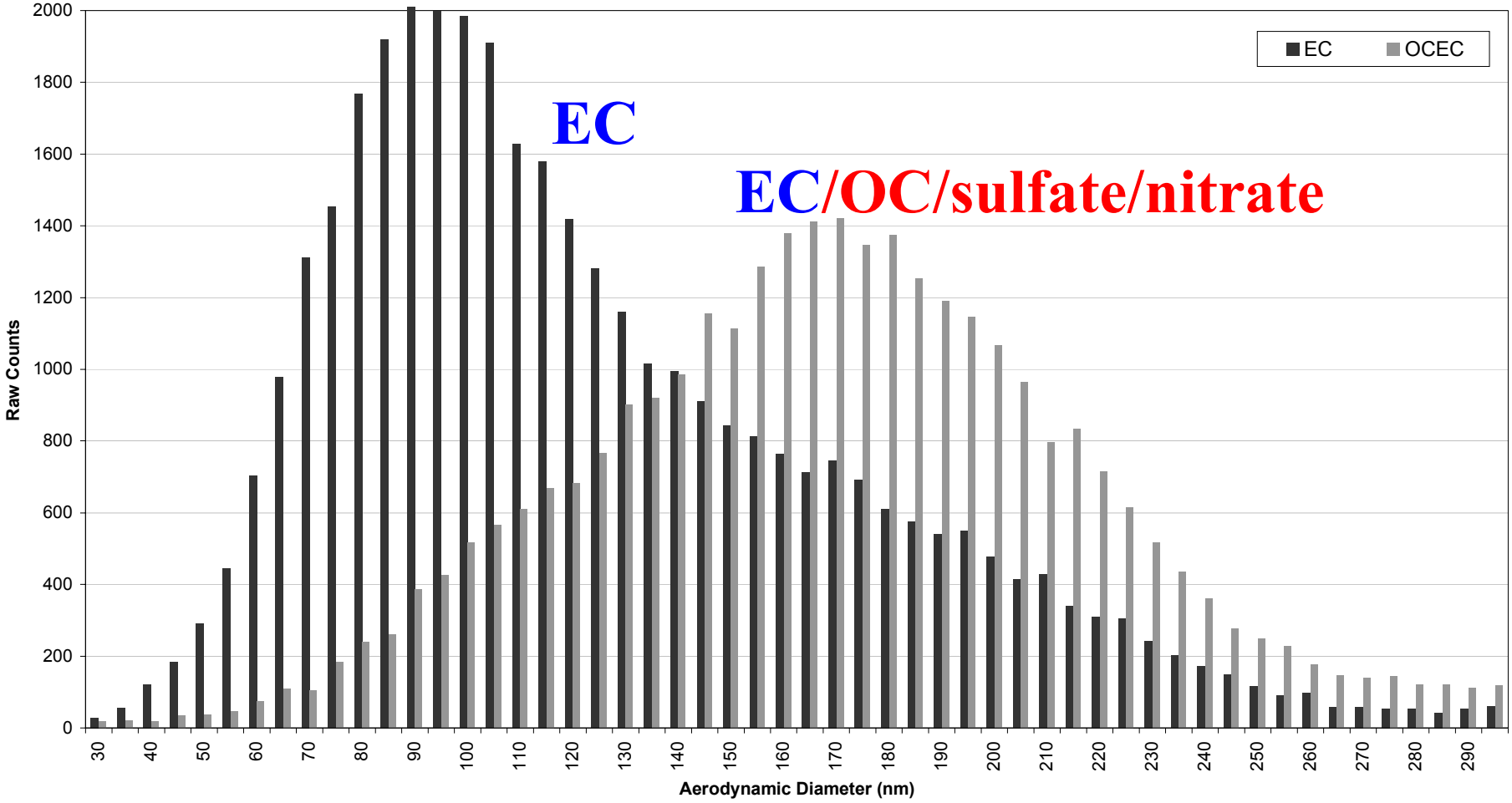
Detection efficiency 1 in 4 at 100 nm


Da = 83 nm
Individual Mass Spectrum
Truck (Diesel) Exhaust
Elemental Carbon (EC)
+
-
C_1^+
C_2^+
C_3^+
$^{40}Ca^+$
HSO_4^-
SO_4^-
Carbon clusters
$C^+, C_2^+, C_3^+, \ldots\ldots C_{15}^+$
Relative Intensity
mass/charge
0
10
20
30
40
50
60
70
80
90
100


Da = 86 nm
Individual Mass Spectrum
Car (Gas) Exhaust
Organic Carbon (OC)
+
-
OC
Relative Intensity
mass/charge
C+
CH3+
NH4+
C2+
27
29
C3+
37
C3H3+
41
43
C4+
C5+
NO3-
HSO4-
0
10
20
30
40
50
60
70
80
90
100


Individual Mass Spectrum
Ambient
OC/EC
+
-
OC
Relative Intensity
mass/charge
C+
CH3+
C2+
27
29
C3+
43
C4+
C5+
NO3-
SO3-
SO4-
HSO4-
0
10
20
30
40
50
60
70
80
90
100

Sizes of EC vs. OC (Ambient)



30 nm → **300 nm**

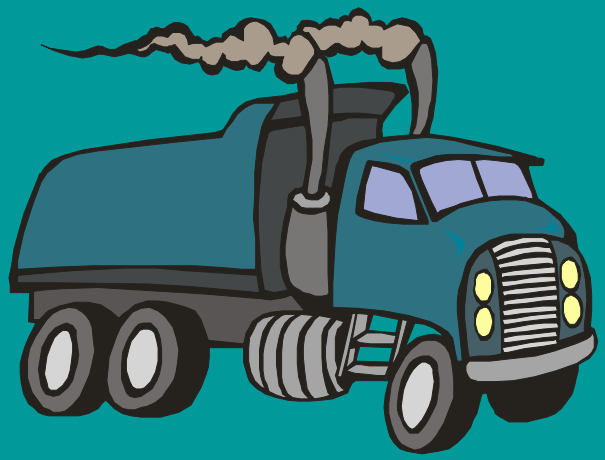
Composition of carbonaceous particles as a function of aerodynamic size

Major Anthropogenic Particulate Sources

Gasoline Vehicles

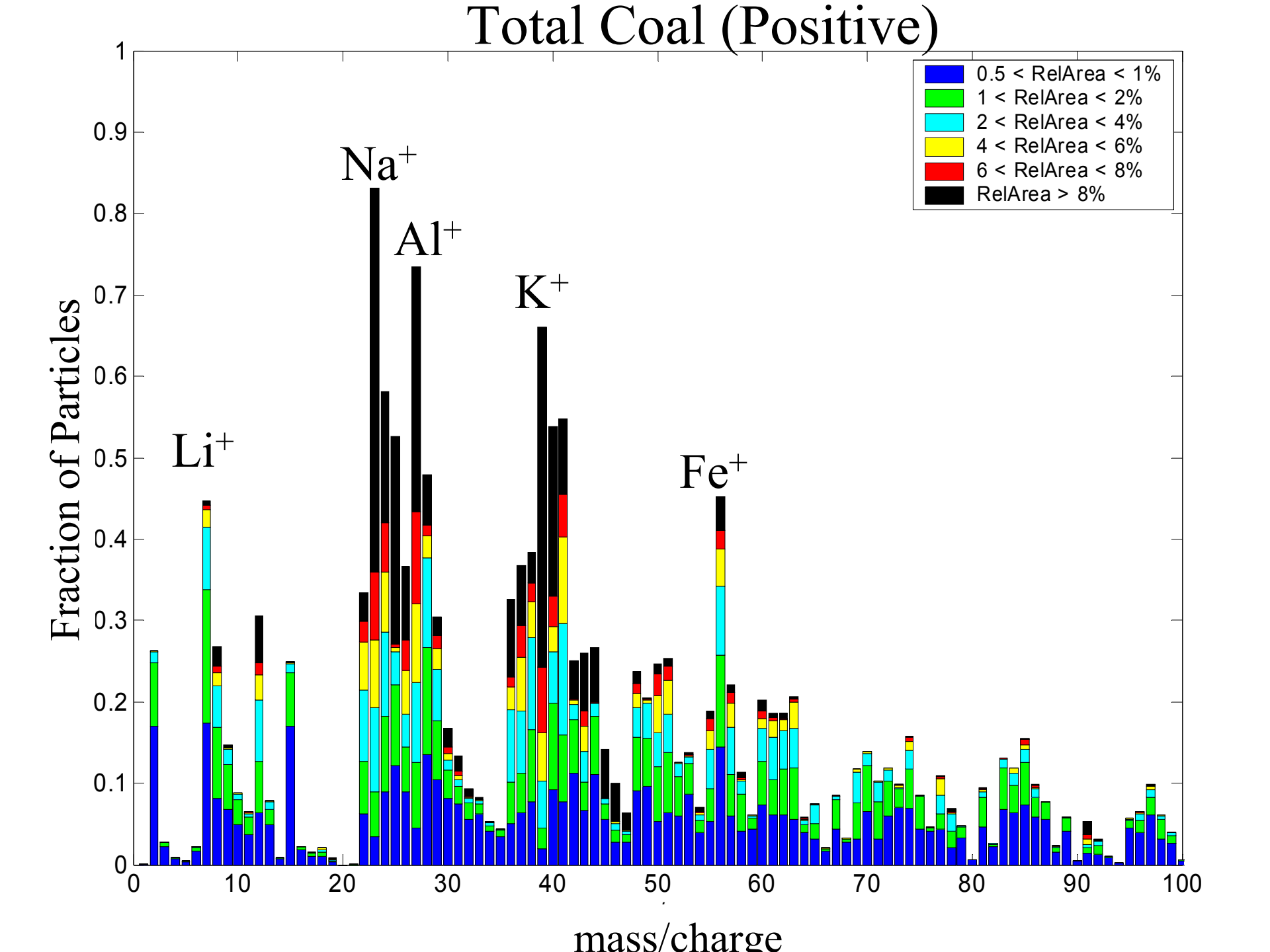
Coal-fired Power Plants

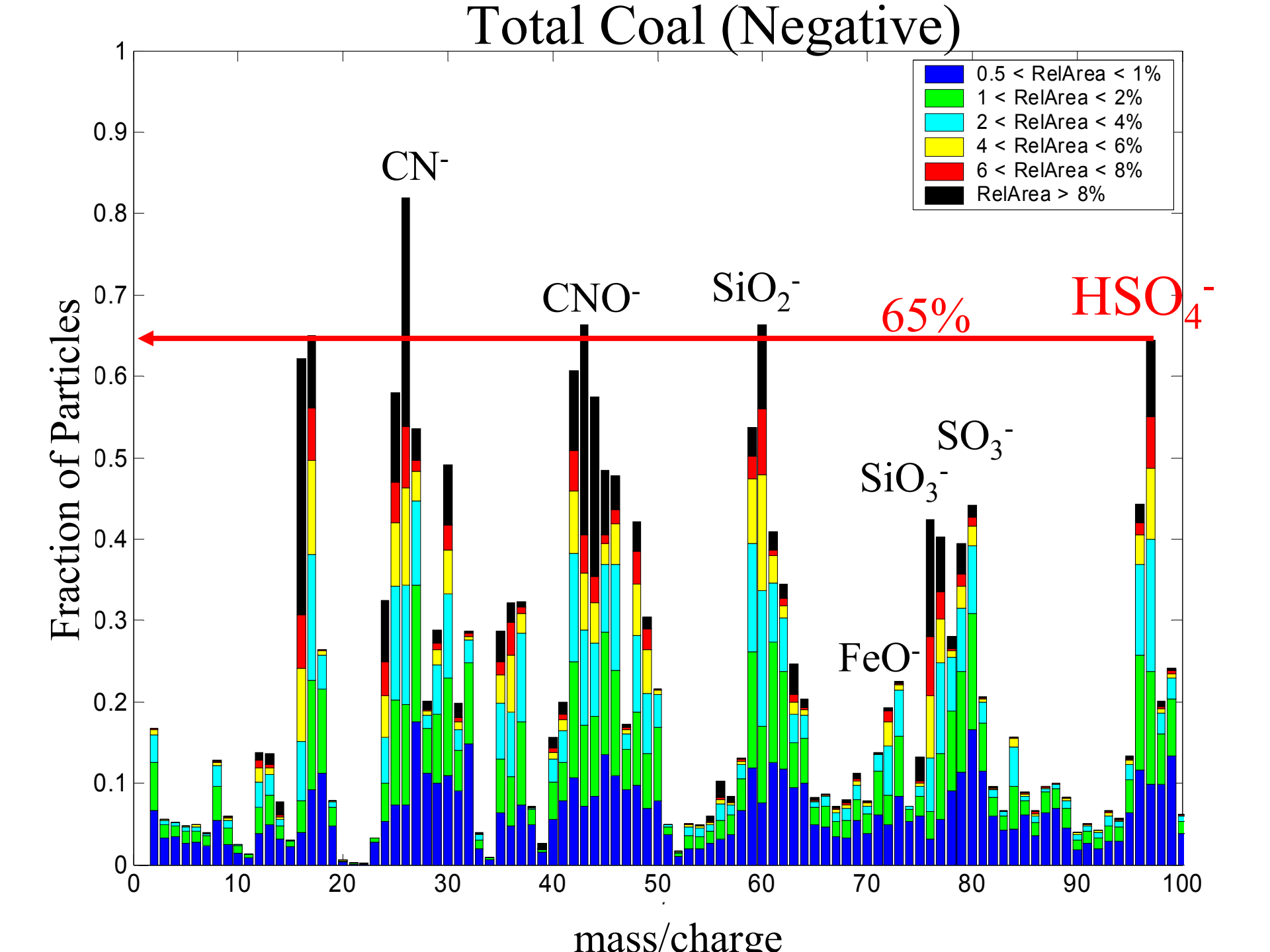
Meat Cooking

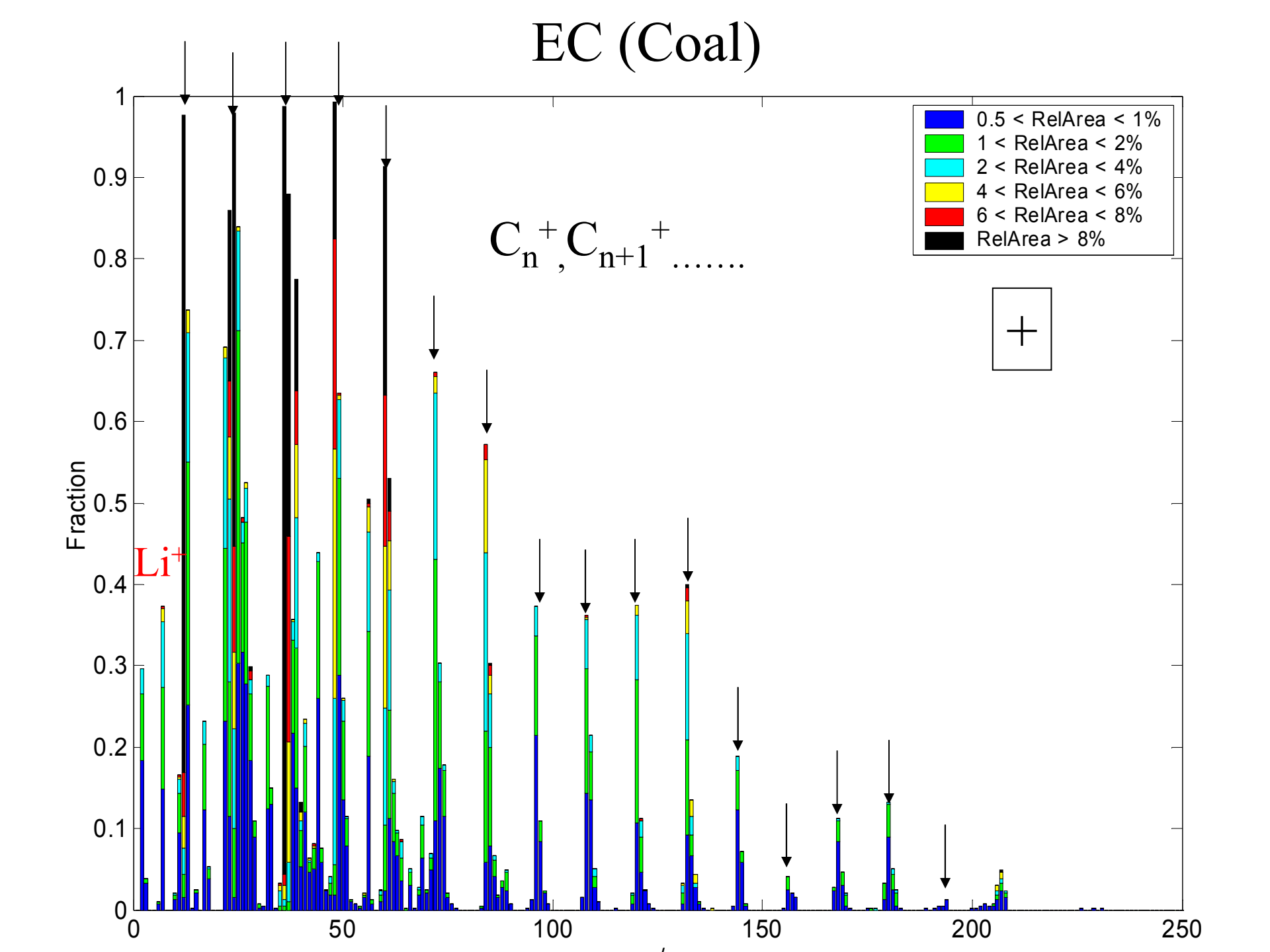


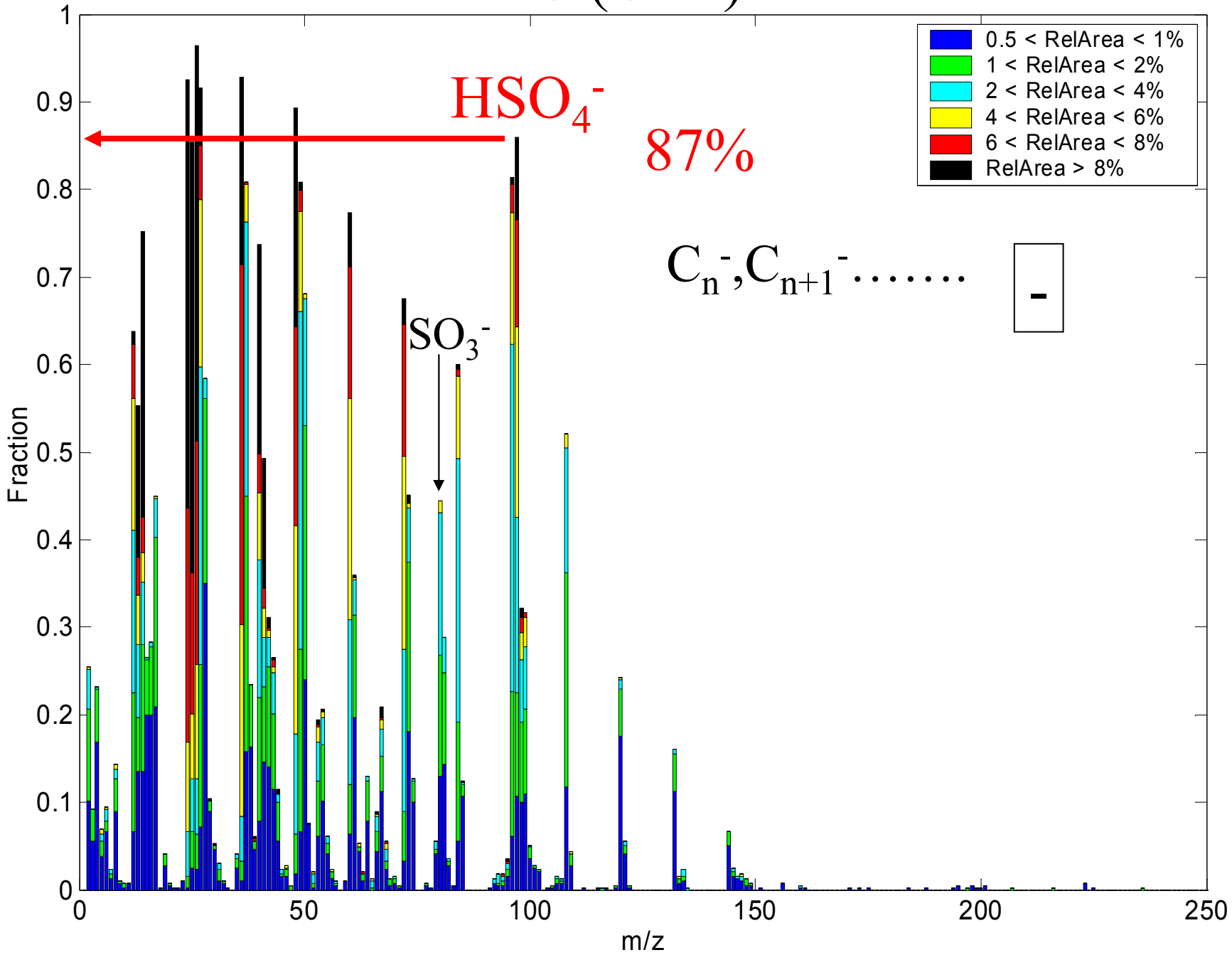
Diesel Vehicles

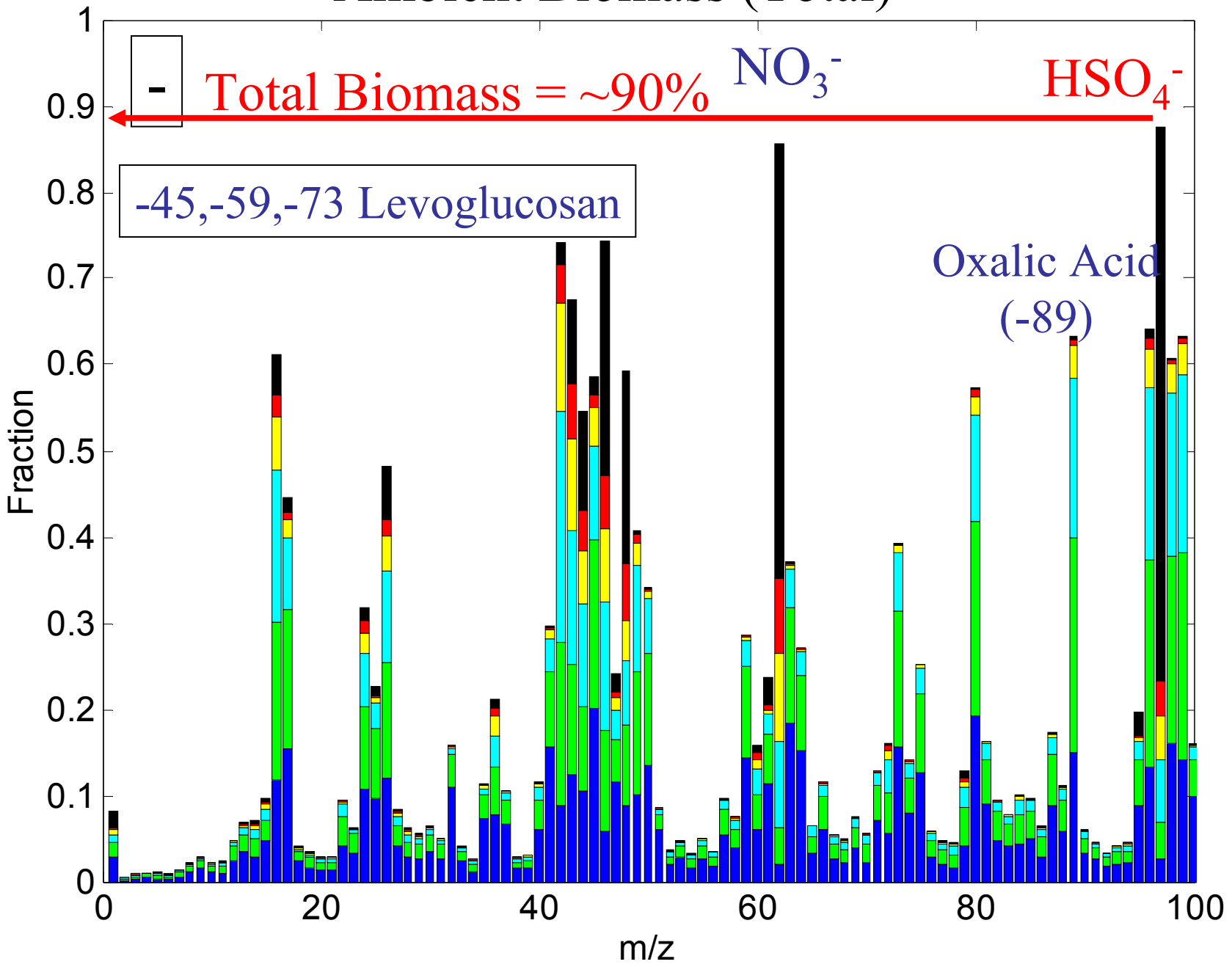
Biomass Burning


Total Coal (Positive)
0.5 < RelArea < 1%
1 < RelArea < 2%
2 < RelArea < 4%
4 < RelArea < 6%
6 < RelArea < 8%
RelArea > 8%
Na+
Al+
K+
Li+
Fe+
Fraction of Particles
mass/charge
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
0
10
20
30
40
50
60
70
80
90
100

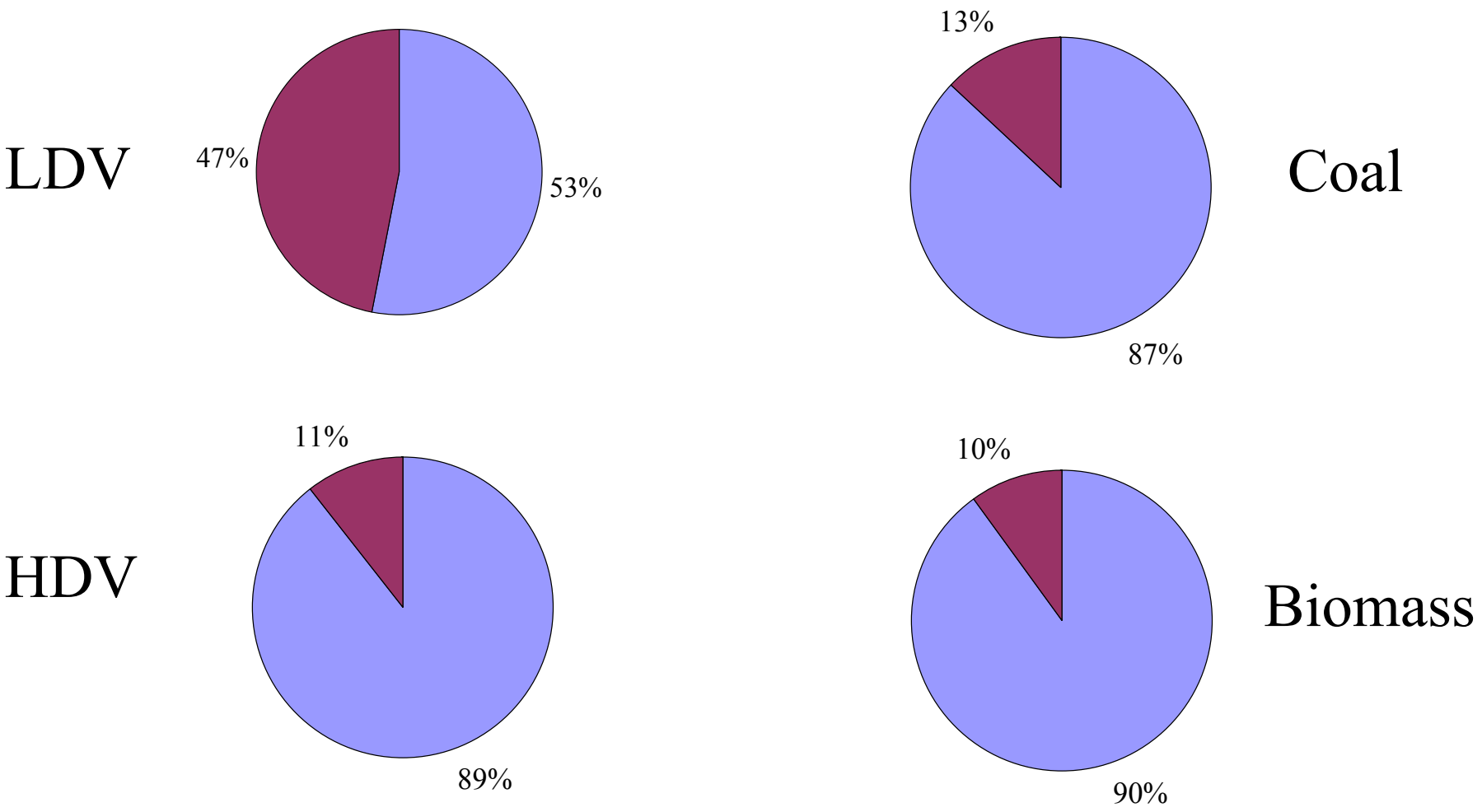

Total Coal (Negative)
0.5 < RelArea < 1%
1 < RelArea < 2%
2 < RelArea < 4%
4 < RelArea < 6%
6 < RelArea < 8%
RelArea > 8%
CN-
CNO-
SiO2-
65%
HSO4-
SO3-
SiO3-
FeO-
Fraction of Particles
mass/charge
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
0
10
20
30
40
50
60
70
80
90
100


EC (Coal)
0.5 < RelArea < 1%
1 < RelArea < 2%
2 < RelArea < 4%
4 < RelArea < 6%
6 < RelArea < 8%
RelArea > 8%
$C_n^+, C_{n+1}^+ \ldots\ldots$
Li+
Fraction
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
0
50
100
150
200
250


EC (Coal)
HSO4-
87%
SO3-
Cn-,Cn+1-.....
0.5 < RelArea < 1%
1 < RelArea < 2%
2 < RelArea < 4%
4 < RelArea < 6%
6 < RelArea < 8%
RelArea > 8%
Fraction
m/z
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
0
50
100
150
200
250

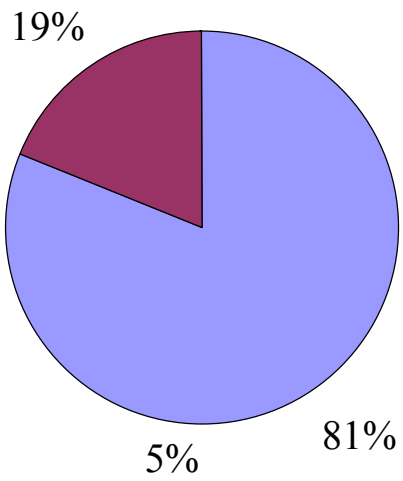

Ambient Biomass (Total)
Total Biomass = ~90%
NO_3^-
HSO_4^-
-45,-59,-73 Levoglucosan
Oxalic Acid
(-89)
Fraction
m/z
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
0
20
40
60
80
100

EC Mixing State—Fresh Emissions (0.1-1 μm)



Ambient EC

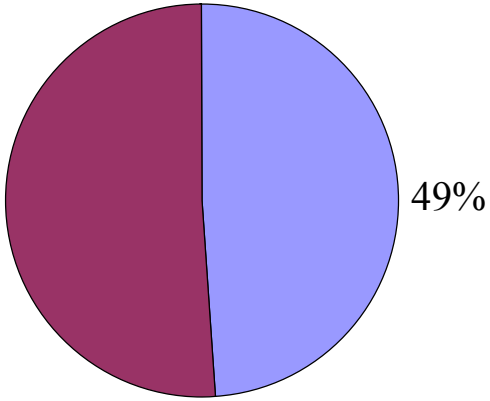
Eastern United States

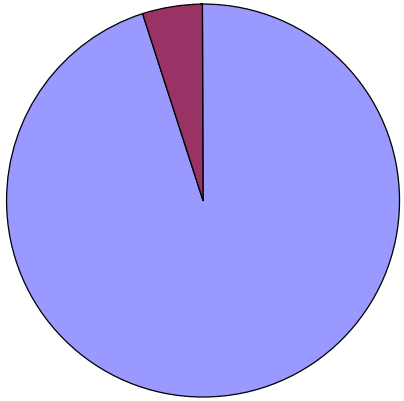


Boston

Western United States

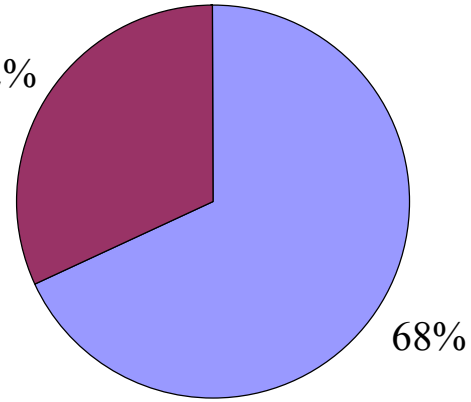
Fresno

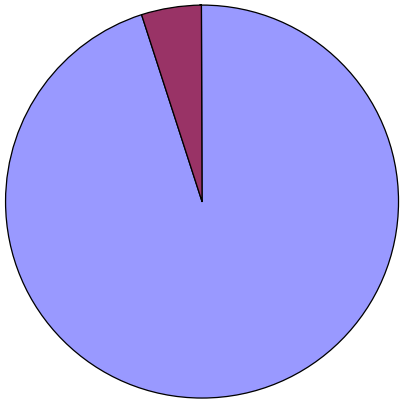




Atlanta

Bakersfield

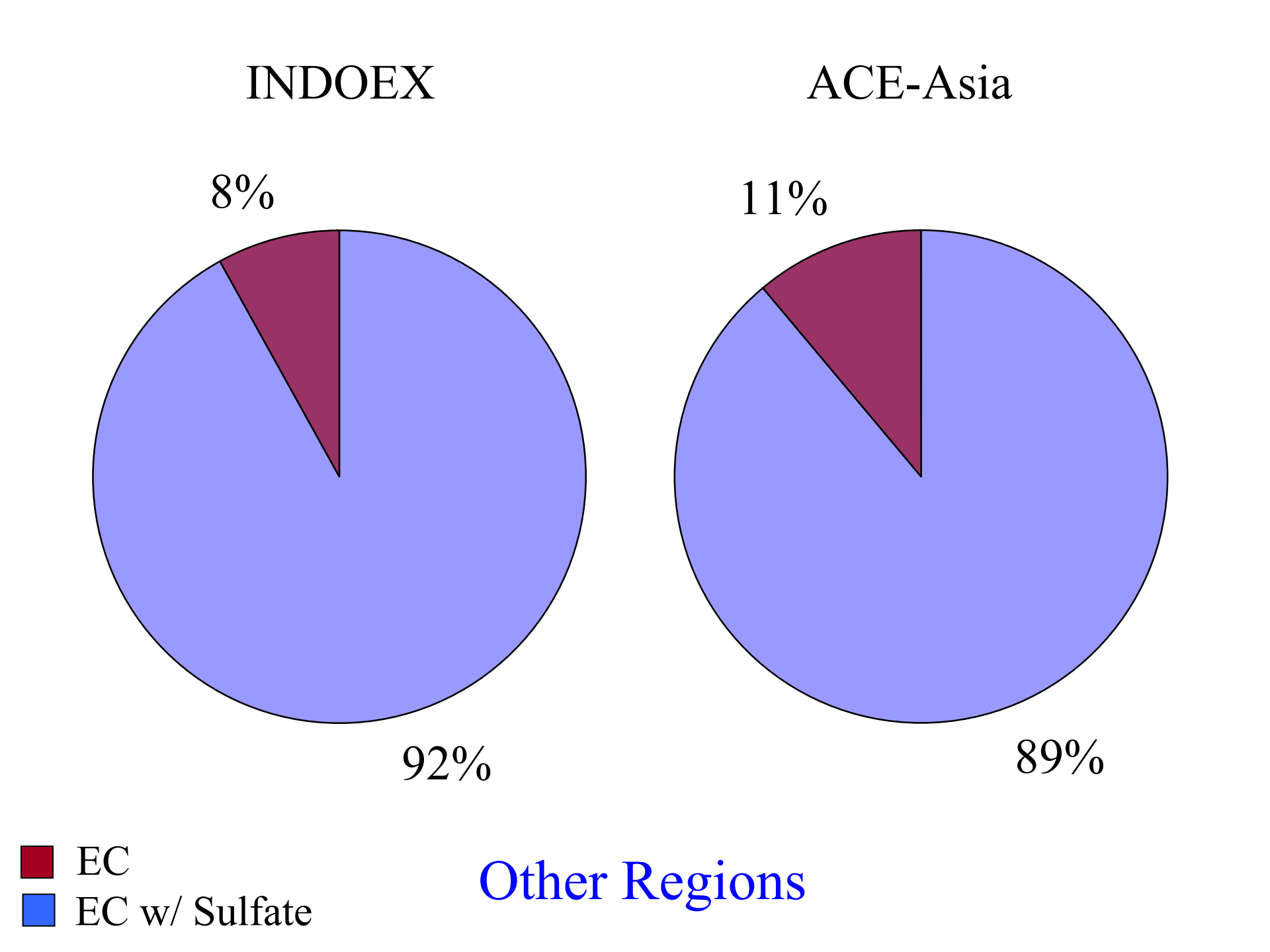




Chapel Hill

EC

EC w/ Sulfate


INDOEX
ACE-Asia
8%
92%
11%
89%
EC
EC w/ Sulfate
Other Regions

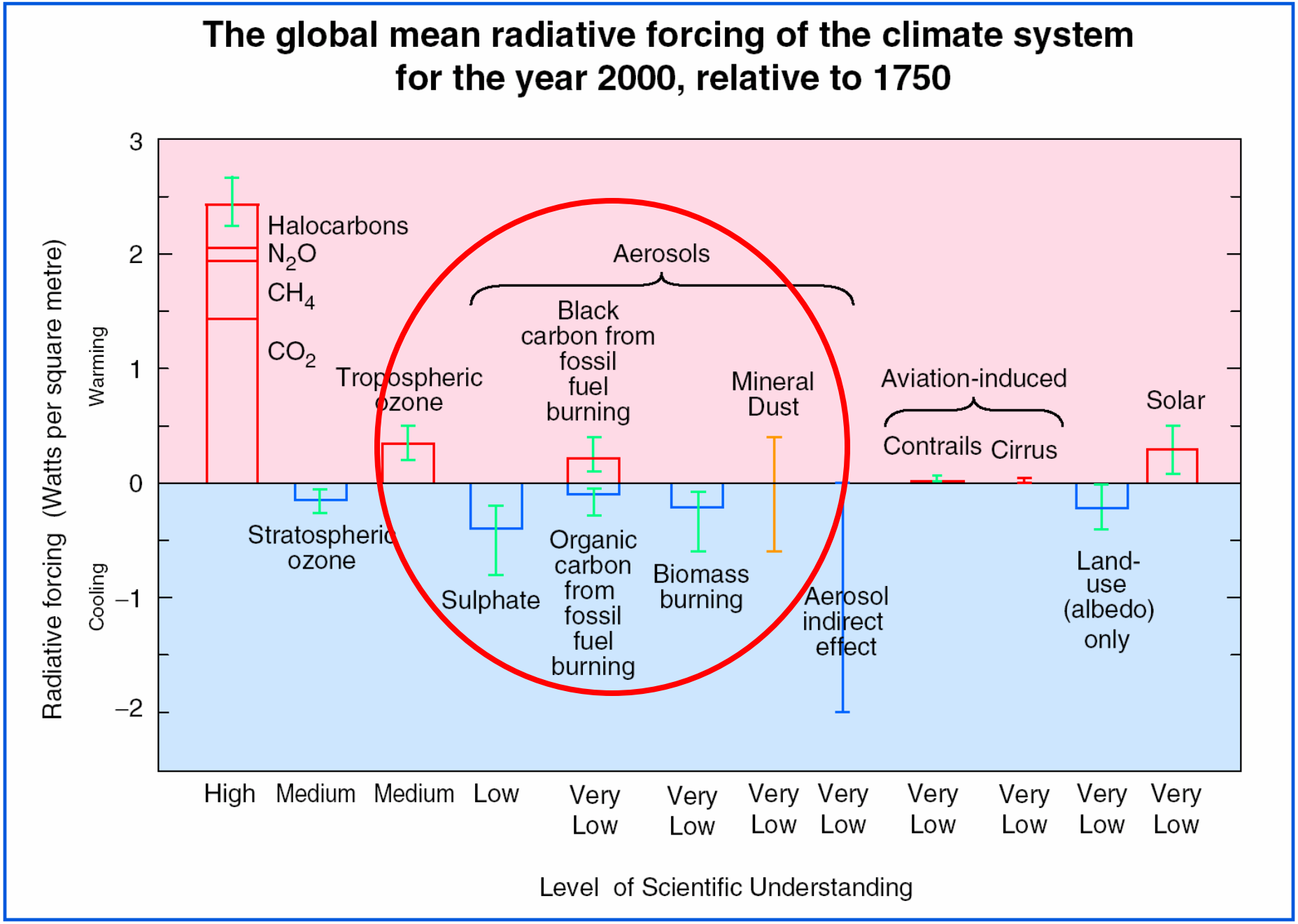


Figure 3: Many external factors force climate change.

* What are the limits in our ability to measure freshly emitted and ambient BC?

What is “BC” and “EC”?

Historically operationally defined

What do we care about? All absorbing species?

Can differentiate between BC from different sources

Has different optical and physical properties

* What are the limits in our ability to determine the sizes and chemical composition of aerosols emitted by BC sources?

Units of size—geometric, mobility, aerodynamic, optical

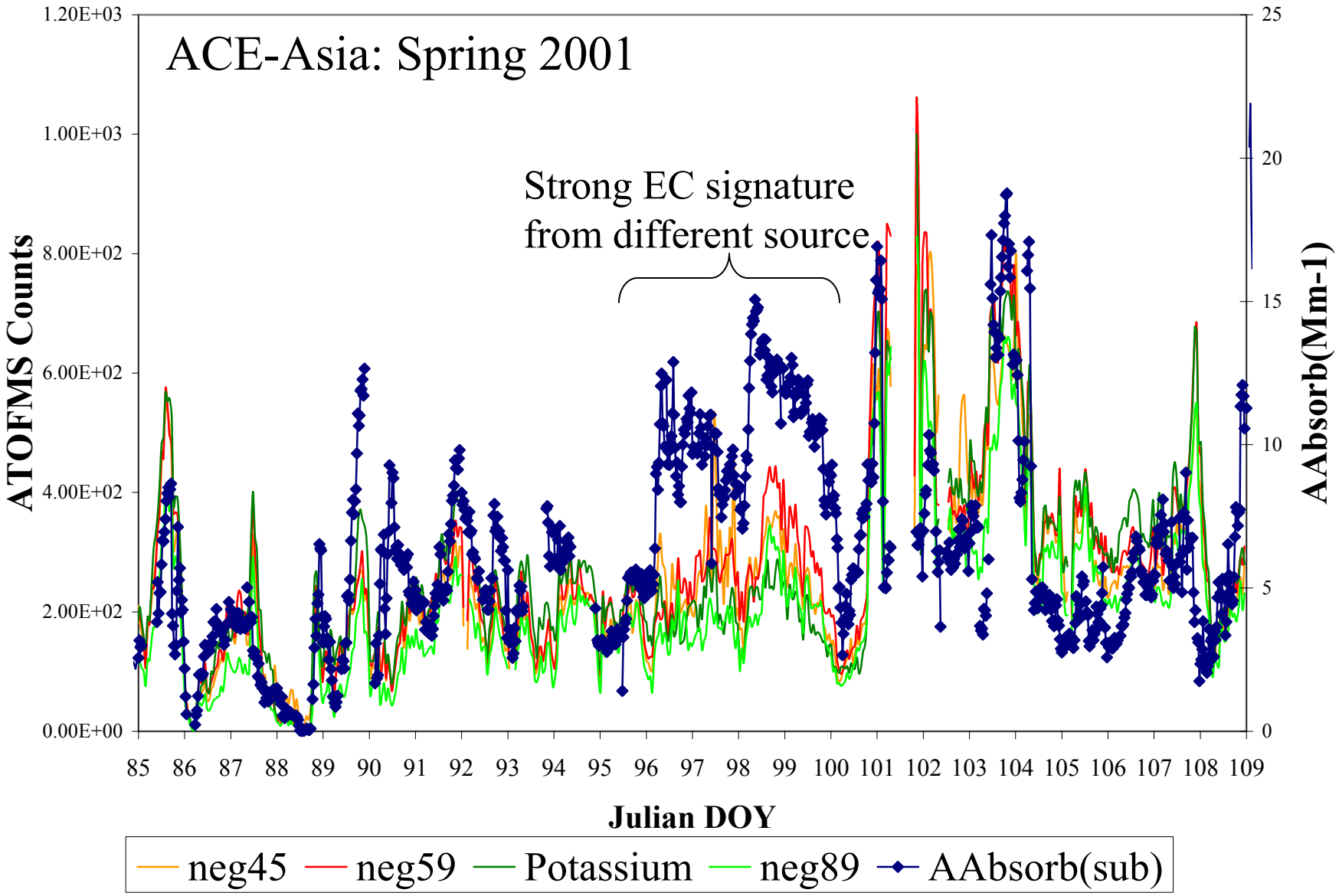
Need size resolved mixing state information

(bulk measurements may be misleading)

Conclusions

- Very important to understand source impact on climate forcing (treating individual species can be misleading)

Atmospheric Absorption versus Biomass



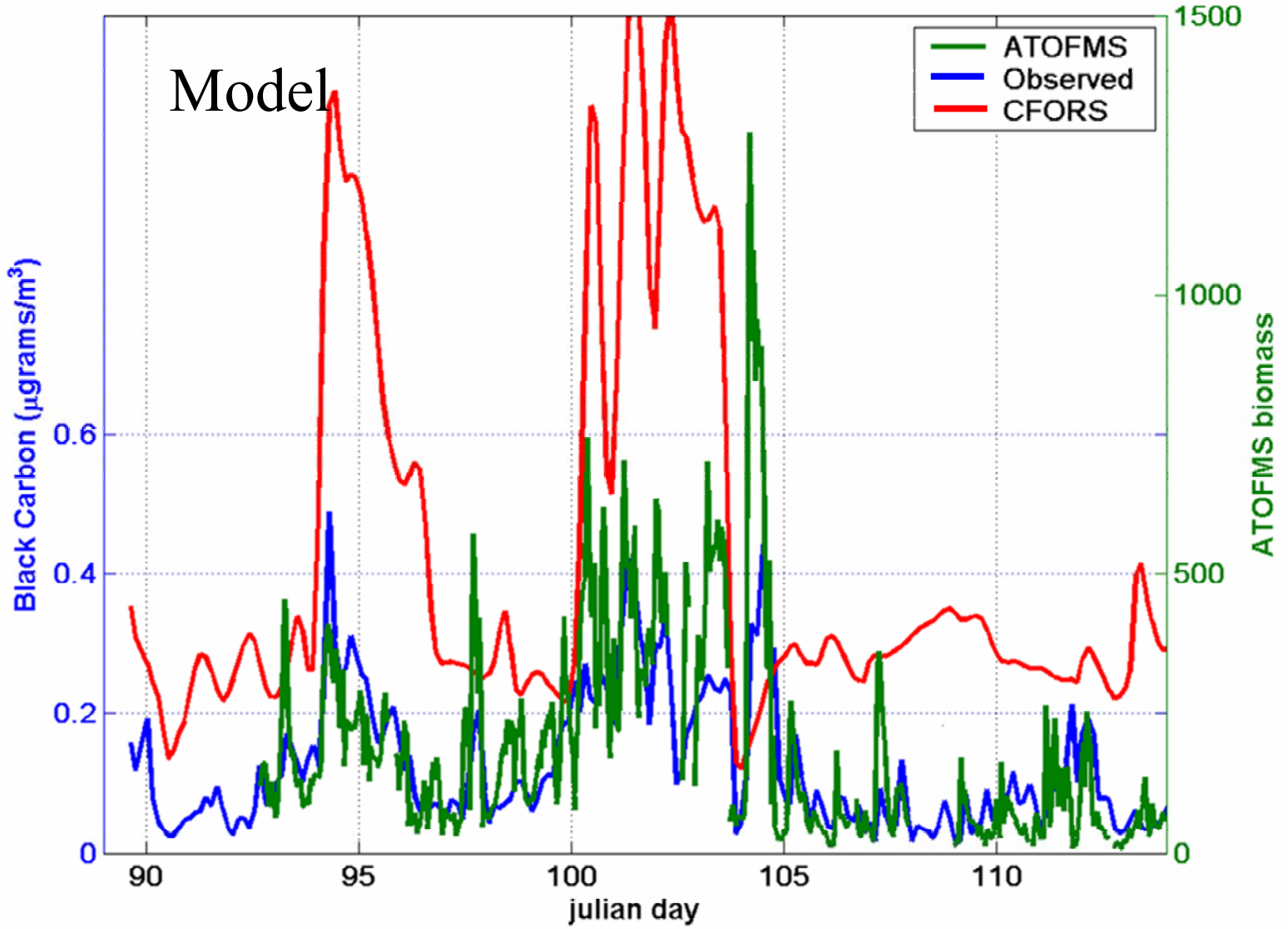
- neg45, neg59, and K (submicron) biomass marker ions

Conclusions

- Suggestion: Target sources producing particles affecting climate with regulations (not just individual species)

- Need better link between measurements and models
  - Provide closure between satellite and ground based measurements, emissions inventories (sources), sinks, important chemical processes

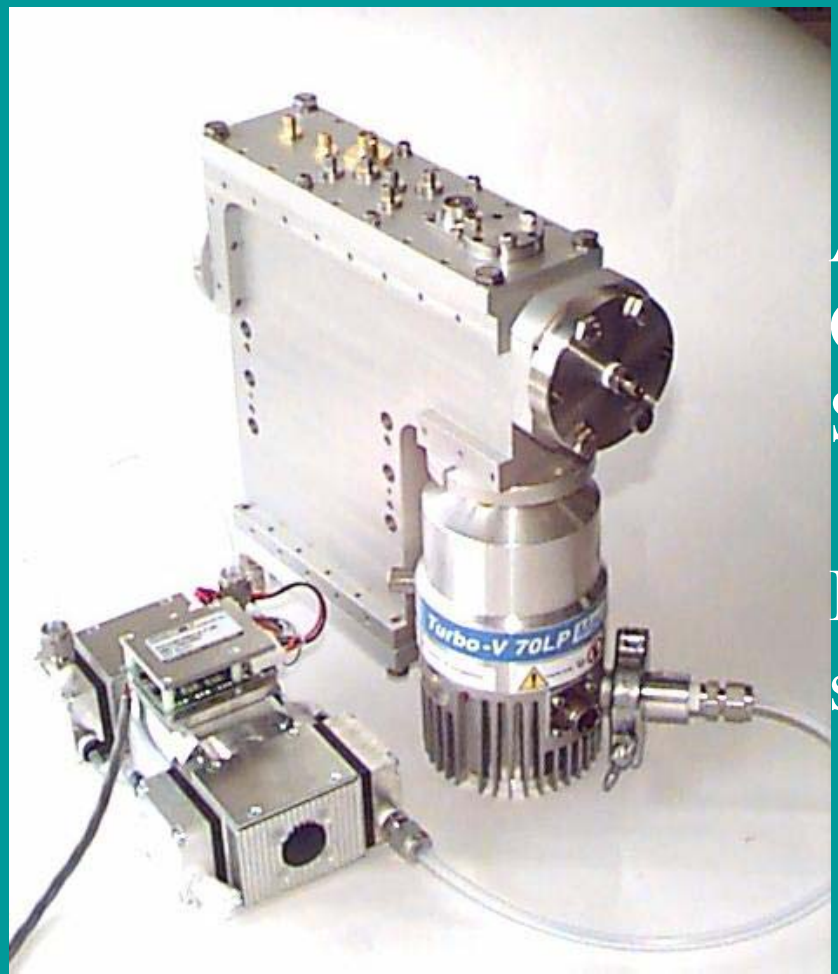
Comparisons (CIFEX; April 2004)



Model and measurement data provided by G. Carmichael and O. Larivie

Compact TOF (Spring 2005)

8.5 x 19 x 2.5 in.
15 lbs. (1 polarity)
Resolution = 5000
m/z 0 to 5000+



Aerodynamic size
Optical size
Single particle composition

Link optical properties directly with sources and aging processes

Acknowledgements

- Brooke, Doug, NREL
- Entire Prather Group (past and present)
- Profs. V. Ramanathan and Paul Crutzen
- Odelle Larivie
- Prof. Greg Carmichael
- Joseph Mayer

- Funding: CARB, EPA, NSF, NOAA, DOE

Prather Group (2003-La Jolla, CA)